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Airborne Mercury in Precipitation in the Lake Superior Region

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16. ABSTRACT

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AIRBORNE MERCURY IN PRECIPITATION IN THE LAKE SUPERIOR REGION

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ABSTRACT. Mercury was measured in accumulated snow (March 1982) sampled from around Lake Superior and in rainfall from Duluth, Minnesota (June–September 1982 and March–November 1983), Forbes Township, and Dorset in northwestern and central Ontario, respectively (May–September 1983). Methods of melting snow and collecting rain samples were investigated to avoid loss of mercury during the melting process and sample shipment and storage. Low concentrations in snow and rain required greater analytical sensitivity. A detection limit of 0.008 ± 0.004 μg/L of mercury (N = 26) was attained using the cold vapor technique; and by utilizing a gold gauze amalgam accessory for preconcentration, a detection limit of 0.005 ± 0.003 μg/L (N = 13) was attained. Regional comparisons of mercury accumulation in the snow pack across the northern parts of Minnesota, Wisconsin, Michigan, and Ontario show highest values, 0.10 ± 0.17 μg/L Hg, in the Grand Rapids, Minnesota, area and lowest values in remote areas of Minnesota and Ontario. Rainfall concentrations of total mercury were substantially higher than snow accumulation and were mainly of inorganic forms (73%). The highest amounts of mercury were measured in rainfall at Duluth, Minnesota (3.4 μg/L) during June 1982 and at Forbes Township, Ontario, (1.2 μg/L) during July 1983. Substantially lower concentrations were observed in the other months of 1982 and 1983. There is no unique association of the observed mercury concentration with the air parcel history. However, the single highest mercury concentration in rainfall observed at Duluth, Minnesota, occurred when the 850-mb air parcel back trajectory indicated upwind corridors to the N-NW and the highest concentration at Forbes Township, Ontario, was associated with an 850-mb trajectory from W-NW. Significant positive correlation coefficients (0.05) were obtained with other measured components in rain at Duluth, Minnesota, including S, B, Ca, Mg, Na, Fe, Mn, and Zn in 1983. Mercury concentrations in precipitation and in lake water for precipitation-dominated lakes are similar and indicate that atmospheric deposition can be the major source of mercury for some lakes in the Lake Superior region.

ADDITIONAL INDEX WORDS: Trace metals, air pollution, acid rain, fallout, atmospheric deposition.

INTRODUCTION

Mercury contamination in fish from Lake Superior and surrounding water bodies has been monitored as the fish exceed the 1978 U.S./Canada Water Quality Agreement objectives (International Joint Commission 1980) and the U.S. Food and Drug Administration's action level of 1 μg Hg per gram of tissue (Hartung and Dinman 1972, Glass and Loucks, 1980, WDNR 1984, MDH 1985, MDNR 1985). Extensive literature is available defining the

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extreme toxicological properties of mercury and its compounds, and environmental health criteria have been established by the World Health Organization (1976). General literature reviews and assessments have been made recently (National Academy of Sciences 1978, Matheson 1979, Galloway *et al.* 1982) and need not be repeated here. Mercury cycles naturally through the atmosphere as part of the hydrologic cycle of water; it is emitted from volcanoes and volatilized from ore bodies as an elemental gas, Hg°. Aerial exploration can be conducted for sulfide ore bodies using mercury gas as a tracer. The sources of acute contamination are generally agreed to be from industrial usage and direct discharge into watersheds and the atmosphere; however, little information is available to define the magnitude and sources of airborne inputs in the Lake Superior region.

The emissions from fossil fuel combustion are significant and add 1,000 kg of mercury/year, on the average, to the atmosphere from each 1,000 mega-watt coal-fired steam-electric plant (Memorandum of Intent 1983, Brosset 1983). Manufacturing processes, especially chlorine at chloralkali plants, have been major sources of air and water emissions (Hogstrom *et al.* 1979). The result is pollutant deposition by dry and wet mechanisms to watersheds and uptake by aquatic organisms (Glass and Loucks 1980). The objectives of this study are to define the existing levels of mercury in precipitation in the Lake Superior region, identify possible source regions, and assess the significance with regard to aquatic resources.

METHODS

Analytical Methods

The method of analyzing mercury in precipitation samples was by cold vapor atomic absorption spectrophotometry (AAS). A selected number of samples were analyzed both with and without deuterium arc background correction in order to verify that no positive spectroscopic interferences (false positive) were present. The methods used for water sample preparation and preservation were published previously by Olson *et al.* (1975) and Feldman (1974).

Snow samples were collected using the methods for estimating snow-pack water content, developed by the Soil Conservation Service (1967), by snow coring along two perpendicular 150-m courses along N-S and E-W axes at each site. Ten snow cores were collected at 15-m intervals along each axis using a coring tube of polypropylene 7.5 cm in diameter and 2 m in length that was pushed perpendicularly through the snow until it reached the ground. The depth of the snow was recorded and the bottom end of the core was inspected; any debris was carefully removed from the bottom of the core with a plastic spatula. Twenty cores per site were composited into a single new polyethylene bag, and protected in transit from punctures by a cotton pillow case. Bags were twisted, taped closed, and labeled. Since snow accumulation will vary with vegetation cover type, coniferous, deciduous, and open areas were sampled using separate courses. Snow composite samples were kept frozen, weighed, and stored in a freezer (-30°C) until analyzed.

Each snow sample was mixed while still in the bag and four replicates of 150 grams were subsampled from each sample bag and placed in 600-mL pyrex beakers. Two of the replicates were each spiked with 3.0 ng of mercury as mercuric chloride ($HgCl_2$). Six mL of 2.5% (W/V) $K_2Cr_2O_7$/25% HNO_3 were dispersed onto the top of the snow samples, and the beakers were covered with aluminum foil and allowed to stand at room temperature until the snow melted.

For each set of four samples, three blanks, five different standards, and an EPA Hg reference standard were analyzed. Two mL of Ultrex HNO_3 and 5 mL of J. T. Baker H_2SO_4 were added to each of the samples, standards, and blanks in carefully cleaned 250-mL pyrex flat bottom flasks used in the analysis and mixed by swirling. Then two mL of 5% (W/V) $KMnO_4$ and 2 mL of 5% (W/V) $K_2S_2O_8$ were added to the flasks, mixed by swirling, and heated on hot plates to near boiling to complete the oxidation of organometallic forms. The flask contents were allowed to cool to room temperature and 2.3 mL of 12% (W/V) hydroxylamine sulfate/12% (W/V) NaCl were added to a flask and swirled until the sample color changed from purple to yellow-green, indicating excess strong oxidants were absent. In the final step of the analyses 5.6 mL of 10% (W/V) stannous sulfate, reductant, were added to the sample flask and it was immediately connected to the cold vapor flameless AAS system for sparging the elemental mercury into a 10-cm light path absorption chamber.

The instrument used for mercury analysis was an atomic absorption spectrophotometer (Perkin-Elmer Corp. model 403) equipped with a deute-

rium arc background corrector. A slit width of 1 mm (spectral band width 0.7 nm) was used at a wavelength of 253.7 nm. The instrument was operated in the concentrations mode with the integration set at 10 average (ten signals averaged as one value every second). The concentration readout of the sample was amplified ten times. The mean concentration of the blanks for the analysis was subtracted from all standards and samples. Mercury concentrations were calculated for all samples using a calibration curve constructed with the blank-corrected standard concentrations, using the program AUTOGC, and a Hewlett-Packard 3350 data system. Analyses of precipitation collected in Ontario were conducted by the Ontario Ministry of Environment's (OMOE) Laboratory Services and Applied Research Branch using similar equipment and techniques (OMOE 1981). The detection criterion for mercury was 0.01 μg/L.

For some samples a gold gauze amalgam attachment (Perkin-Elmer Corp.) was adapted for use with the cold vapor system. It was connected to a variable autotransformer (Staco Energy Products Co., Dayton, Ohio) and a time delay relay (Model 328MOS Automatic Timing and Controls Co., King of Prussia, Pennsylvania) so that each sample was aerated for 60 seconds; then the gold gauze amalgam was heated by 13.0 volts (550–600°C) for 55 seconds with vacuum pressure applied to the absorption cell 25 seconds after heating began. An air stream was used to cool the gold gauze to room temperature (3 minutes) between samples. An improvement in sensitivity and reproducibility was observed if, after each day's use, the gold gauze was removed and soaked in 10% HNO_3 for 15 minutes, then rinsed in deionized, distilled water and dried.

Analyses of pH, conductivity, and acidity were conducted when sufficient sample volume was available using Radiometer Corporation digital titrator (model TTT81, with ABU80 autoburett and pHM64 pH meter), and employing methodology of standard methods (APHA 1981). Analyses of additional elemental components, metals, sulfur, and phosphorus were conducted using a Bausch and Lomb inductively coupled plasma emission spectrophotometer, model QA-137, equipped with vacuum UV capabilities and a 1 meter spectrometer (1,920 g/mm grating). The methodology employed for these analyses are described in detail in Method 200.7 (USEPA 1979).

Sampling Methods

Rainfall and wind direction/velocity during rainfall were monitored on the grounds and roof of the Environmental Research Laboratory-Duluth (ERL-D) by using an Aerochem Metrics Wet/Dry Precipitation Sampler (Aerochem Metrics Inc., Bushnell, Florida) connected to a Belfort Weighing Raingauge (Belfort Instrument Co., Baltimore, Maryland) and a Weathertronics Recording Wind System (Qualimetrics Inc., West Sacramento, California); see Figure 1. Rain falling on the sensor of the Aerochem Metrics sampler activated the cover to move from the wet side "bucket" to the dry side. This event was marked separately on the recorder chart of the rain gauge along with the amount of rainfall measured. The wind direction and velocity were recorded on the chart of the wind monitoring system.

Rain samples for mercury analyses were collected by placing four 600-mL pyrex beakers containing 3 mL of 2.5% (W/V) $K_2Cr_2O_7$-25% HNO_3 (to give a final concentration at 150 mL sample of 0.05% $K_2Cr_2O_7$-0.5% HNO_3) side by side in a circle inside the "wet side" bucket of an Aerochem Metrics collector (Fig. 1). Funnels were placed in each of the beakers to minimize dry uptake and splashing during a heavy rainfall. Samples were generally collected for individual rainfall events which rarely exceeded 50% of the volume of the collection beakers. Samples containing less than 150 mL were increased to that volume with distilled water, in the analyses flask. In Ontario, polyethylene bags were used as bucket liners. Depending on the sampling periods, a 500-mL preservative solution of 0.06% $K_2Cr_2O_7$ and 1% HNO_3 was added before sampling or 2 mL of a saturated $K_2Cr_2O_7$ and 2 mL of concentrated HNO_3 were added as a preservative after sampling. The Ontario results are to be considered as qualitative.

Lake water samples were obtained from 19 lakes using a Kemmerer water sampler at 1 meter below the lake surface and 1 meter above the lake bottom. Each sample was split between two or four 250-mL polyethylene bottles, each containing 3 mL of $K_2Cr_2O_7$ HNO_3 preservative. Each replicate was split and analyzed for total and inorganic (undigested) mercury.

Air Parcel Trajectory Calculations

On days on which ERL-D precipitation mercury analysis results for individual events were available

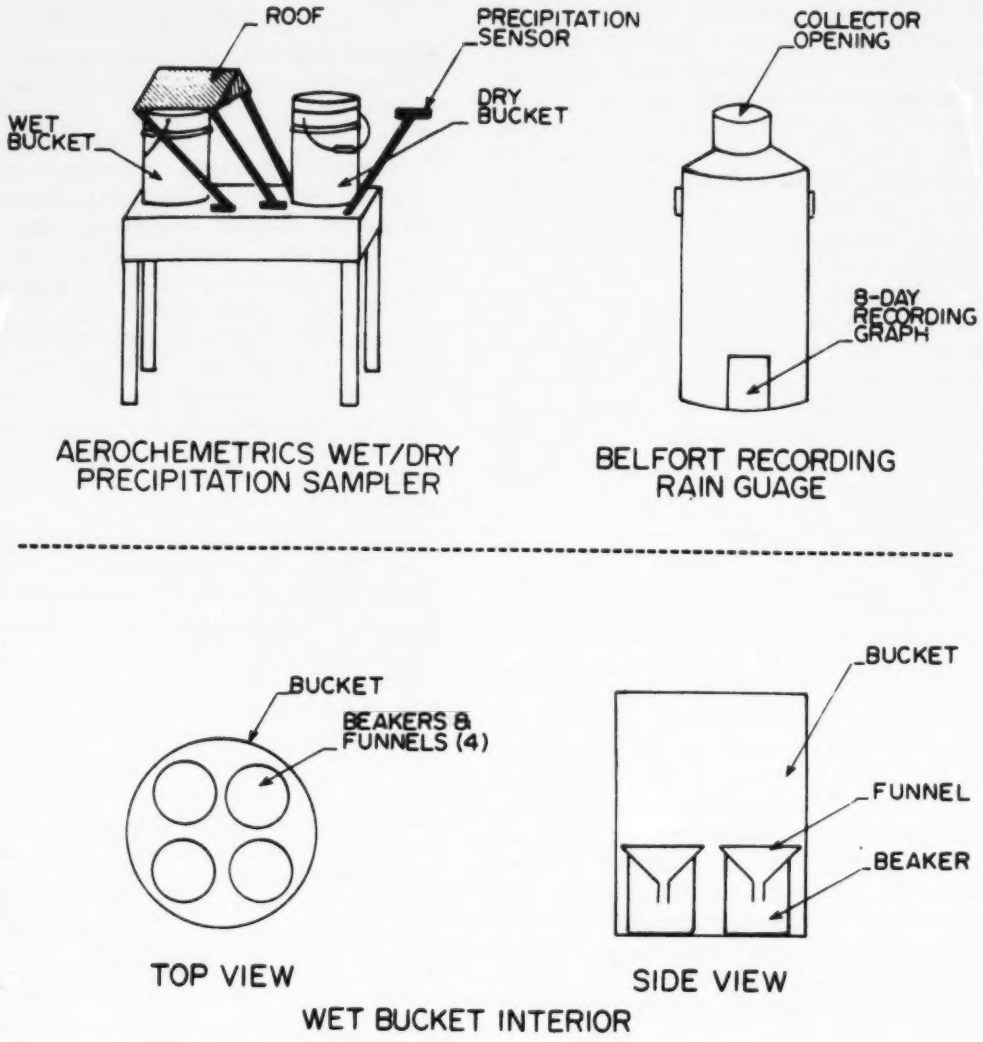

FIG. 1. Precipitation monitoring and collection equipment used in the study of mercury.

during 1982 and 1983, "modified" surface geostrophic and 850-mb air parcel back-trajectories were calculated from Duluth and Forbes Township for a 48-hour period using the trajectory model of the Air Resources Branch, Ontario Ministry of the Environment. For the "modified" surface geostrophic back-trajectories, the wind direction was backed by 15° and the wind speed was decreased by 10%. Neglecting motions of acceleration, representative horizontal winds (u and v components) in the atmospheric boundary layer were obtained from the surface and 850-mb geostrophic winds, with modifications for surface frictional effects, using three-hourly synoptic weather data from approximately 300 stations in a 30 × 30 grid system (grid length 127 km) for the surface level and using the height fields on a 11 × 11 grid system (grid length 381 km) for the 850-mb level. To obtain air parcel trajectories originating at a specific location, the three-hourly wind vectors (surface) and the twelve-hourly wind vectors (850 mb) were integrated with forward time-steps over 48

hours (see description in Petterssen 1956). Trajectories beyond this time period were not projected since air flows then are likely to be subjected to significant deformation. Trajectories derived in this manner are in good agreement with low-level tetroon observations (Peterson 1966). The 850-mb level trajectories are probably better than the surface geostrophic trajectories because they are closer to those calculated using a multi-level model.

RESULTS AND DISCUSSION

Methodological Aspects

Sampling/Recovery—Due to the difficulties in making low level quantitative measurements of mercury in environmental samples, several methodological aspects of the analyses were investigated. Quantitative aspects of rain sample collection were checked using both glass and plastic funnels and sample bottles, with and without oxidant. The most consistent results were obtained using either plastic or glass containers, with the $K_2Cr_2O_7/HNO_3$ preservative added to the container *before* collecting samples (Fig. 1). The presence of the preservative can also increase the contribution to the rain sample from dry or gaseous deposition depending upon air concentrations and exposure time in the sampler. This can make a significant difference if a long time period has elapsed between rain events.

The concentrations of mercury in water from melted snow varies substantially depending upon the conditions under which the snow is melted. Experiments were conducted to determine the most reliable conditions for analysis and recovery of mercury that was spiked into the snow before melting. Table 1 shows the results of varying the melt conditions, the recovery of spiked mercury samples and quality assurance agreement with "known" samples. These results indicate that highly variable analyses will result if the oxidant is not added to the snow directly before melting. As a precaution against false negative results and to check for variation/contamination with storage time, a large snow sample was selected to be subsampled and spiked for recovery during the analyses of each batch of samples. The results (Table 1) show that no loss occurred over several months of storage

TABLE 1. Mercury analyses variations on snow treatment and results of known samples.

Sample, Sequence of Additions		Number of Replicates	Recovery, Mean	Standard Deviation	Specified Level of Hg
Snow + $K_2Cr_2O_7$–HNO_3 + 0.003 μg Hg[a]		53	97%	22.0	
Snow + $K_2Cr_2O_7$–HNO_3 + 0.006 μg Hg[a]		6	118%	19.8	
Snow + $K_2Cr_2O_7$–HNO_3 + 0.010 μg Hg[a]		16	94%	16.0	
Snow + 0.010 μg Hg + $K_2Cr_2O_7$–HNO_3[b], melted		3	54%	4.9	
Snow + 0.010 μg Hg, melted + $K_2Cr_2O_7$–HNO_3		4	54%	13.0	
Snow-bulk sample[c]		19	<0.013 μg/L	0.002 μg/L	
Snow-bulk sample + Hg Spike, 0.170 μg/L[c]		21	0.180 μg/L	0.009 μg/L	0.170 μg/L
Reagent Blanks	(1982)	210	0.006 μg/L	0.0021 μg/L	
	(1983)	69	0.003 μg/L	0.0017 μg/L	
Minimum Detectable Concentration	(1982)	36	0.013 μg/L	0.003 μg/L	
	(1983)	26	0.008 μg/L	0.004 μg/L	
	(Amalgam)	13	0.005 μg/L	0.003 μg/L	
EPA Reference Standards (Hg)		1	0.024 μg/L		0.028 μg/L
		1	0.032 μg/L		0.042 μg/L
		26	0.052 μg/L	0.003 μg/L	0.052 μg/L
		8	0.050 μg/L	0.003 μg/L	0.056 μg/L
		4	0.070 μg/L	0.005 μg/L	0.084 μg/L
NBS Standard #1642b		11	0.044 μg/L	0.003 μg/L	0.042 μg/L

[a] $K_2Cr_2O_7$–HNO_3 (preservative) added across snow surface in beaker after Hg spike across snow surface.

[b] $K_2Cr_2O_7$–HNO_3 (preservative) in beaker before snow + Hg spike added across surface.

[c] A large sample of snow (bulk sample #82TCK071E51060) was melted. One half of the melted sample was spiked with a known amount of mercury. Then the sample was preserved by adding $K_2Cr_2O_7/HNO_3$ and both were kept at 4°C. An aliquot was analyzed with each batch of samples for the evaluation of instrumental and time variations of analyses.

and that highly reproducible results were attainable.

Interferences—Four sets of replicate rain samples and an EPA mercury standard reference sample were analyzed both with and without deuterium arc background correction to measure for positive interferences. Four of the five comparison data sets showed higher mercury values (+22%) when using background correction than when not using background correction. However, these differences were within the variability of the method used and indicate no significant positive interferences were present in the samples checked. The use of background correction required operating the mercury electrodeless discharge lamp (EDL) at about a thirty percent lower power setting in order to balance the EDL's intensity with the intensity of the deuterium arc background corrector. This caused a loss of sensitivity and raised the concentration level of detection by 3.5 times when using this method for background correction. The values from both modes of analyses agreed reasonably well with 15% ± 10% for the precipitation samples and with 11% variation for the EPA mercury reference standard samples.

In order to obtain a lower detection limit for the mercury analysis of precipitation samples, a gold gauze amalgam cell from the MHS-20 Mercury/Hydride System (Perkin-Elmer Corp.) was added to the existing cold vapor analyses system by splicing it in-line, before the $Mg(ClO_4)_2$ drying tube. This allowed the mercury vapor to be concentrated on the gold gauze and vaporized into the light path in a more concentrated state. Air was pumped through the sample, sparging it for 60 seconds, and the mercury vapor was trapped on the gold gauze amalgam cell. A time delay relay switched on a variable autotransformer supplying 13.0 volts for 55 seconds to the gold gauze to heat it rapidly to 600°C. After 25 seconds of heating, a vacuum was applied to the outlet side of the light absorption cell to draw the volatilized mercury through the absorption cell to complete the analysis before heating ceases and the gauze was purged of mercury by the remainder of the heating cycle. Cooling air was then circulated through the exterior of the cell to cool it to room temperature before analyzing the next sample.

The instrument response (10X concentration mode, arbitrary units) versus mercury concentrations in 150-mL sample volumes for the three different methodologies are given by the linear regression equations in the form y = constant + slope (χ). The (±) values are one standard deviation.

Instrument response = 2.75 (±0.55) + 1,120 (±8) [Hg μg/L], (cold vapor) blank = 0.006 μg/L;

Instrument response = 1.65 (±12) + 6,560 (±194) [Hg μg/L]; (gold amalgam) blank = 0.006 μg/L;

Instrument response = 30 (±20) + 15,200 (±330) [Hg μg/L], (improved gold amalgam) blank = 0.002 μg/L.

Comparing the cold vapor and gold amalgam methods, there was an increase of 1.17 times in instrument response for standard solutions of mercury relative to the response for the blank sample. A similar comparison for the improved gold amalgam yielded an increase of 1.79 times over the blank and showed a significant overall increase in sensitivity and a lowering of the detection limit. From these data it was evident that the detection limit of a method improves only when the blank value is lowered for the analysis. If further effort was put into lowering the blank value of the analysis a significant improvement in detection limit could be achieved, but for the present work the detection limit allowed analysis of all but one sample, c.f. Table 4.

Precision/Accuracy—The results of analyses to assess the precision and accuracy of mercury determinations are given in Table 1 for standard and environmental samples. A snow sample (from Hovland, Minnesota) was spiked with a known amount of mercury to measure recovery and variation over time. This spiked sample was analyzed with each batch of samples and the results showed 0.183 ± 0.009 μg/L Hg for 21 different analyses. The unspiked snow sample had a Hg concentration of 0.013 ± 0.002 μg/L for 13 analyses. In checks of accuracy, EPA reference standards for mercury were analyzed with each sample set at each concentration level of analysis used for environmental samples and gave consistent values in the 80–100% range of the certified or "true" value. In an additional test for accuracy, the analysis of the national Bureau of Standards standard sample (number 1642b) gave results which agreed within 5% of the certified value (Table 1).

Detection Limit—The minimum detectable concentration was calculated by the IUPAC method which assumes that the major source of error is in the blank and is equal to the mean concentration of the blank plus three times the standard deviation of the blank (Winefordner and Long 1983). For the ERL-D methods used this was 0.013 μg/L for 36 sample sets (1982, cold vapor) and 0.005 μg/L for 13 sample sets (1983, gold amalgam) for a 150-mL sample (Table 1).

Total and Inorganic Forms of Mercury—Five sets of rain samples collected at ERL-D during September and October of 1983 were analyzed for both total mercury and inorganic mercury. Reduction with stannous chloride after digestion with acidic permanganate was shown (Ure 1975) to release organic and inorganic mercury, while reduction with no prior digestion released only the inorganic forms of mercury. The organic forms of mercury can be inferred by difference. The fraction of the inorganic mercury compared to the total mercury for five precipitation events ranged from 0.54–0.80. The mean fraction of inorganic mercury forms was 0.73 ± 0.11 (Table 2). This is in sharp contrast with the findings of Brosset (1983), who reported total and inorganic mercury in rain and snow in Sweden and found that the inorganic fraction of mercury was 0.1–0.2 of the total mercury concentrations, but consistent with our measurements of mercury concentrations and inorganic forms found in nineteen "precipitation dominated" seepage lakes in north-central Wisconsin. Total mercury concentrations measured in precipitation and lakes within the Lake Superior region are shown in Table 2 with selected values form the literature for comparison. These data are discussed in detail below.

TABLE 2. Total mercury concentrations and inorganic fraction measured in precipitation and lake water with selected literature values.

Sample Type, Location	Date	Mercury Concentration, Total, μg/L			Fraction Inorganic		Reference
		Mean	Range	Number of Samples	Mean	Range	
RAIN/SNOW							
ERL-D	5/82–9/82	0.310	0.010–3.40	14			
Duluth, MN, U.S.A.	3/83–11/83	0.050	0.004–0.22	30			
46°50′18″ 92°00′18″	9/83–10/83	0.025	0.009–0.040	4	0.73	0.54–0.80	
Forbes Twsp.	5/83–9/83	0.24	0.01–1.22	15			
NW Ontario, Canada			<0.01	16			
48°34′58″ 89°38′56″							
Dorset	5/83–9/83	0.021	0.01–0.04	12			
Central Ontario, Canada			<0.01	11			
45°13′23″ 78°55′49″							
Lake Superior Region (Fig. 2)	3/82 Snow cores	0.026	0.012–0.10	63			
Cape Cod, Massachusetts, U.S.A.	9,10/75	0.011	0.006–0.018	4			Fogg and Fitzgerald 1979
Avery Point, Connecticut, U.S.A.	3,11/75	0.012	0.003–0.017	5			Fogg and Fitzgerald 1979
Sweden	1981–1982		0.050–0.100			0.10–0.20	Brosset 1983
Hakodate, Japan	12/74–11/75		0.001–0.002	60			Matsunaga and Goto 1976
LAKES							
Northcentral Wisconsin, U.S.A.	7/83–9/83						
Surface water		0.074	0.018–0.245	19	0.83	0.67–1.0	
					(0.55	0.48–0.62)[a]	
Bottom water		0.050	0.013–0.134	19	0.83	0.54–1.0	
					(0.79	0.63–0.97)[a]	
Lake Superior at ERL-D Intake		0.007	<0.004–0.010	9	0.2		Glass 1977

[a]Fraction of total mercury passing 0.45 μ Millipore filter.

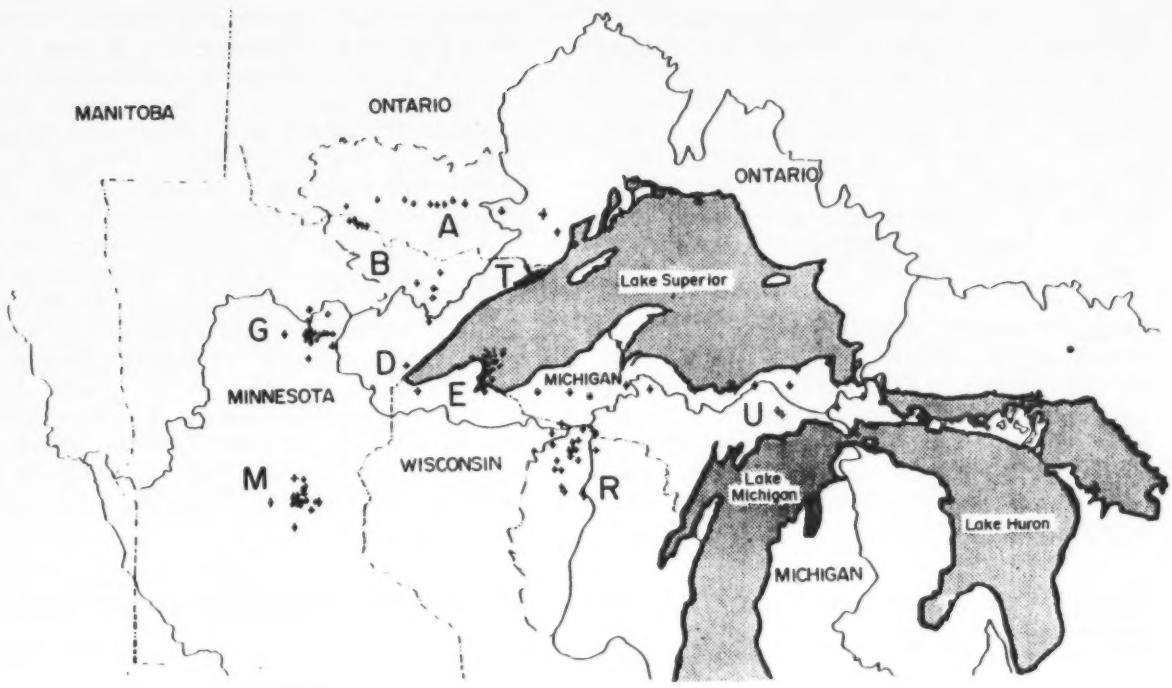

FIG. 2. Snow coursing sites for sampling accumulated water and mercury during March 1982 in the Lake Superior region. Watershed boundaries are also indicated.

Mercury Accumulation in Snow: Regional Distribution

Snow pack sampling provides an excellent opportunity to determine regional differences in atmospheric deposition due to the relative ease of obtaining synoptic samples. Snow pack accumulation of mercury, H^+, and H_2O from 63 sites sampled in March 1982 are shown in Figure 2 and the data are summarized in Table 3. For most of the sampling sites the mercury concentrations were at or near the 1982 detection limit (0.013 μg/L), except central Minnesota where concentrations in the Grand Rapids, Minnesota area compared to other areas suggest local sources, but regional levels are generally low and compare with literature values (Table 2) for remote areas.

TABLE 3. Concentration of mercury, pH, and water content of snow sampled in March 1982.

Region Sampled	pH Snow, Melted	Snow Density kg/10³ cm³	Mercury Concentration[a] (μg/L)	Number of Samples <D.L.	Number of Samples >D.L.	Detection Limit Mercury μg/L X ± 1 S.D.
A (Atikokan, Ont.)	5.46	0.169	0.014 ± 0.001	15	2	0.013 ± 0.001
G (Grand Rapids, MN)	5.21	0.231	0.100 ± 0.173	3	13	0.012 ± 0.003
M (Monticello, MN)	5.76	0.291	0.015 ± 0.005	6	5	0.013 ± 0.001
T (Hovland, MN)	4.65	0.208	0.015 ± 0.004	9	4	0.013 ± 0.001
R (Rhinelander, WI)	4.61	0.231	0.012 ± 0.003	6	4	0.011 ± 0.003
U (U.P., MI)	4.69	0.220	<0.013[b]	12	0	0.013 ± 0.001

[a]Mean values are computed using the total number of sample analyses with an estimate value of 1/2 the detection limit (D.L.) value given to those samples falling below the instrumental detection limit for that particular analyses; ± 1 S.D.

[b]Samples melted without $K_2Cr_2O_7/HNO_3$ added.

Event Variations of Mercury and Other Components in Precipitation

The results of the analyses of forty-four precipitation events during 1982–1983 at ERL-D, Duluth, Minnesota, (Table 4) and Forbes, Ontario (Table 2) show surprisingly high concentrations in rain in comparison with snow accumulations. All of the mercury concentrations in 44 rain samples from Duluth, Minnesota, were above the detection limit of 0.013 μg/L Hg in 1982 and 0.008 μg/L in 1983, except two. These concentrations averaged 0.133 ± 0.51 μg/L, n = 44, with a high of 3.38 μg/L and a median value of 0.037 μg/L. Two consecutive events in June 1982 were 10 and 70 times higher than the mean of all others measured in the 2-year period. At Forbes, Ontario, where measurements were begun in May 1983, 31 rain events were measured (Table 2) with results similar to those shown for Duluth except that the highest concentration of 1.22 μg/L Hg occurred in July 1983.

Twenty three rain events were also monitored at Dorset in southeast Ontario in 1983; and lower concentrations were observed compared to Duluth and Forbes, ranging from less than 0.01 to 0.04 μg/L Hg (Table 2). All of the above observations show the high degree of variability that seems to characterize the mercury-in-rain observations reported in the literature (Table 2). Several explanations could account for the extreme variations observed at both Duluth, Minnesota, and Forbes, Ontario, over the 2-year period of study including: a) three or four air masses of high mercury concentrations; b) conditions of high conversion rates of mercury vapor to soluble and/or particulate forms were coincident with precipitation events; and c) the observed washout reflected relatively homogeneous atmospheric concentrations and/or uniform conversion rates, but increases in point-source emissions occurred.

Possible Sources/Mechanisms: Air Parcel Back-Trajectories

In an effort to determine possible sources (or source regions) of airborne mercury, air parcel corridors were computed for each precipitation event. The surface geostrophic air parcel back-trajectories for up to 48 hours from ERL-D (Duluth) showed the predominant sections of origin were NW and SW for the highest concentrations and the lowest from the S, W, and NE sectors (Table 4, Fig. 3). The magnitude of the mercury concentrations appeared to be related to both the sector of origin of the air parcel and the time of the year. The highest value measured at Duluth in June, 1982, had air parcel movements from the N-NW sector for both sampling events at the surface and 850-mb levels. These values were not repeated in June, 1983, but the air parcel movements were from the S to W essentially (for the entire month) at both surface and 850-mb levels. But at Forbes, Ontario, the highest value was observed in July, 1983, when the air parcel origin was from the W-NW sector. The pathways of the air parcel movements are shown in Figure 3 for the individual eight rain events at ERL-D where the mercury concentrations were the highest (upper half) and the lowest. It is evident that there is no unique association of the observed mercury concentration with the air parcel history. It should be noted that additional precipitation events and periodic releases may have occurred (with resultant washout) along the back-trajectory corridors, hence preventing a definitive determination of sources at that time.

The observed variability of mercury concentrations in rain are consistent with observed variability in air concentrations (Lindqvist *et al.* 1984) and atmospheric residence times estimated to be less than or equal to 0.4 years. The significant differences between winter snow concentrations and accumulations and rain concentrations in the spring and summer suggest differences in scavenging mechanisms but are also consistent with the observations of Brosset (1981, 1982) that oxidants, which are much more abundant in the spring and summer, play a key role in mercury deposition by oxidation of gaseous elemental mercury to compounds that are more effectively scavenged and deposited by precipitation events.

Mercury Correlation Analyses With Other Components in Precipitation

Measurements of other components in rain samples from 1983 were made in a preliminary attempt to determine possible source signatures (Rahn 1981). A summary of the data is shown in Table 5 for 28 event samples. A correlation matrix is shown in Table 6 for these data with mercury concentrations and event volume. The statistical significance of these relationships is given in terms of three levels of confidence. No correlation coefficient is shown for a given pair of parameters if the statistical significance is less than 90% confidence level (Table 6) of being different from zero.

Mercury concentrations show statistically signif-

TABLE 4. Precipitation sampling, meteorological conditions, and mercury concentrations at ERL-D, Duluth, Minnesota.

Sampling Event: Date, Time, Location[a]			Precipitation: Rain (cm H_2O)	Surface Wind: Direction/ Velocity, km/hr	Air Parcel Trajectory: Code, Predominant Factor(s), Surface, 850 mb	Mercury Concentration, μg/liter	Days Beakers[b] In AeroChem Sampler	Analysis Date
13-5-82:	0500–1530:	F	1.27	E-8	1, SE, S	0.018 ± 0.003[c]	1	14-5-82
16-5-82:	0500–0830:	F	1.27	E-24	2, SE, S	0.023 ± 0.004	3	17-5-82
9-6-82:	1345–1530:	F	1.27	ESE-16	3, SE, SW/S	0.015 ± 0.004	24	10-6-82
18-6-82:	1230–1730:	F	1.27	WSW-16	4, NE, N	3.376 ± 0.268	9	22-6-82
29-6-82:	1240–2045:	R	2.54	NW-8	5, N/NE, NW/(N)	0.512 ± 0.054	11	30-6-82
5-7-82:	2245–2400:	R	2.54	ESE-16	6, S/SW, SW	0.098 ± 0.010	6	06-7-82
6-7-82:	0000–0645:	R	3.81	WSW-16	7, SW, SW	0.037 ± 0.006	1	08-7-82
8-7-82:	1730–2400:	R	4.57	E-16-24	8, W/NW, W/NW	0.039 ± 0.004	2	13-7-82
15-7-82:	1500–1830:	R	2.54	E-16	9, S, SW	0.050 ± 0.005	7	16-7-82
24-7-82:	0615–1000:	R	4.32	SW-16	10, S/SE, SW	0.034 ± 0.002	9	27-7-82
29-7-82:	0430–1500:	R	2.54	NW-8	11, SW/W/NW, NW	0.061 ± 0.004	5	30-7-82
13-8-82:	0330–0730:	R	3.05	SE-8	12, S, SW	0.030 ± 0.300	15	16-8-82
10-9-82:	0430–1230:	R	5.33	SE-16	13, S, SW	0.026 ± 0.002	28	30-9-82
22-9-82:	0330–1800:	R	3.81	WSW-8-16	14, SW/W, W/NW	0.010 (0.002)	12	30-9-82
7-3-83:	1000–1800:	R	1.5 Snow[d]	N-24-32	15, SE/S, S	0.051 (0.006)	1	21-3-83
8-3-83:								
22-3-83:		R	Dry Absorption[e]			[0.113 (0.015)]	15	29-3-83
31-3-83:	0100–0500:	R	1.52	NNE-8	16, S, SW	0.166 (one)	9	01-4-83
1-4-83:	1700–2400:	R	0.38	N-8-16	17, E, SE/S	0.023 (0.007)	1	05-4-83
			Dry Absorption			[0.034] (N = 1)	1	05-4-83
6-4-83:	1300–1500:	R	0.38	ENE-16-24	18, E/NE, E/NE	0.075 (0.030)	5	13-4-83
			Dry Absorption[f]			[0.098] (N = 1)	7	13-4-83
13-4-83:	1800–2200:	R	0.38	NNE-24-48	19, E/SE, SE/S	0.007 (0.002)	7	13-4-83
14-4-83:	0400–1200:	R	0.09 Snow[d]	NNW-8-16	20, NE/E/SE, E/SE/S	0.009 (0.003)	1	15-4-83
19-4-83:	0300–0400:	R	0.5	E-8-24	21, SW/S/SE/E, NW	0.042 (N = 1)	4	20-4-83
28-4-83:	0600–0800:	R	0.64	ESE-8	22, NW, W/NW	0.106 (0.014)	14	04-5-83
	1300–1500:	R						
12-5-83:	1800–2200:	R	1.78	ENE-16-24	23, SE, S	0.044 (0.005)	14	18-5-83
18-5-83:	1800–0600:	R	0.64	ENE-16-32	24, SE, S	0.140 (0.058)	6	25-5-83
22-5-83:	0100–0400:	R	0.50	NNW-8-32	25, S, W	0.220 (0.020)	4	25-5-83
28-5-83:	0400–1000:	R	1.02	E-8-16	26, SE, NW/W	0.018 (0.000)	12	01-6-83
29-5-83:	0100–1200:	R						
30-5-83:	1200–1800:	R						
3-6-83:	0400–1200:	R	1.02	NNE-8	27, S, S/(SW)	0.052 (0.004)	4	08-6-83
4-6-83:	0400–1000:	R						
14-6-83:	0100–1200:	R	1.27	NNE-8-16	28, S, S	0.106 (0.011)	11	15-6-83
15-6-83:	0600–1000:	R	0.89	ESE-0-8	29, W, W/NW	0.017 (0.002)	1	21-6-83
26-6-83:	0400–0600:	R	0.51	NNE-24-40	30, SW, W/(SW)	0.124 (0.016)	11	29-6-83
30-6-83:	1800–0100:	R	1.40	ESE-0-8	31, SW/S, W/SW	0.016 (0.004)	4	05-7-83
01-7-83:	1100–1300:	R						
3-7-83:	0900–2300:	R	5.97	W-24-40	32, S, SW	0.004 (0.002)	3	05-7-83
16-8-83:	1100–1400:	R	1.64	NNW-8	33, S, W	0.036 (0.010)	44	17-8-83
29-8-83:	0900–1200:	R	3.18	WSW-24-32	34, SW/(W), W/(SW)	0.044 (0.006)	13	30-8-83
4-9-83:	1200–1900:	R	0.89	WSW-16-24	35, W, SW	0.038 (0.006)	6	08-9-83
10-9-83:	0000–0400:	R	3.05	WSW-24-32	36, SW, W/SW	0.014 (0.001)	6	13-9-83
11-9-83:	1200–2300:	R	0.25	ENE-8-16	37, NW/N, NW	0.065 (0.008)	1	16-9-83
15-9-83:	0300–2400:	R	3.56	ENE-24-32	38, SE(E), S	< 0.004 (0)	4	19-9-83
29-9-83:	1100–2400:	R	1.02	ENE-8-16	39, S/(SE,E), SW	0.038 (0.003)	14	30-9-83
			Dry Absorption[e]			[0.020] (N = 1)	1	30-8-83
30-9-83:	0000–0200:	R	1.27	ENE-8-16	40, S/SE, S	0.030 (0.003)	1	06-10-83
			Dry Absorption[e]			[0.006] (N = 1)	1	06-10-83
10-10-83:	1200–1600:	R	1.04	ENE-16-24	41, S/SE/E, SW	0.008 (0.002)	10	12-10-83
14-10-83:	0000–0400:	R	2.16	ENE-16-24	42, N/NE, N	0.011 (0.003)	4	18-10-83
19-11-83:	0600–2400:	R	0.43	W-24-57	43, SE/S, S	0.004 (0.000)	6	21-11-83
28-11-83:	0300–2400:	R	3.94 Snow[d]	NE-33-65	44, NE, E/SE	0.007 (0.002)	Grab Sample	1-12-83

[a]Location of sample collector: F represents the field behind ERL-D and R represents the rooftop of ERL-D.

[b]Time beakers in AeroChem Metrics sampler – represents the number of days in which the four 600-mL pyrex beakers (containing 3 mL of $HNO_3/K_2Cr_2O_7$) were inside the AeroChem Metrics sampler before a rain event occurred.

[c]Hg μg/liter, mean value ± S.D. – represents a mean of four replicate samples (n = 4) plus or minus one standard deviation.

[d]Snow sample: represents two replicates of new snow, sampled (150 g each) on the ERL-D roof. Water content assumed to be 10% of the snow volume.

[e]Dry absorption was estimated on occasions where no rainfall had occurred. The pyrex beaker with funnel contained 3 mL of $HNO_3/K_2Cr_2O_7$ preservative for an exposure period of the days indicated. The surface area of the beaker bottom (preservative covered) was about 31.4 cm2. Values reported were for samples collected on the "wet side" of the AeroChemetrics sampler.

[f]Dry absorption was estimated as in 7 with samples collected on the "dry side" of the AeroChemetrics sampler. First rain, necessary to activate the collector's sensor, is probably included with the amount described as "dry absorption."

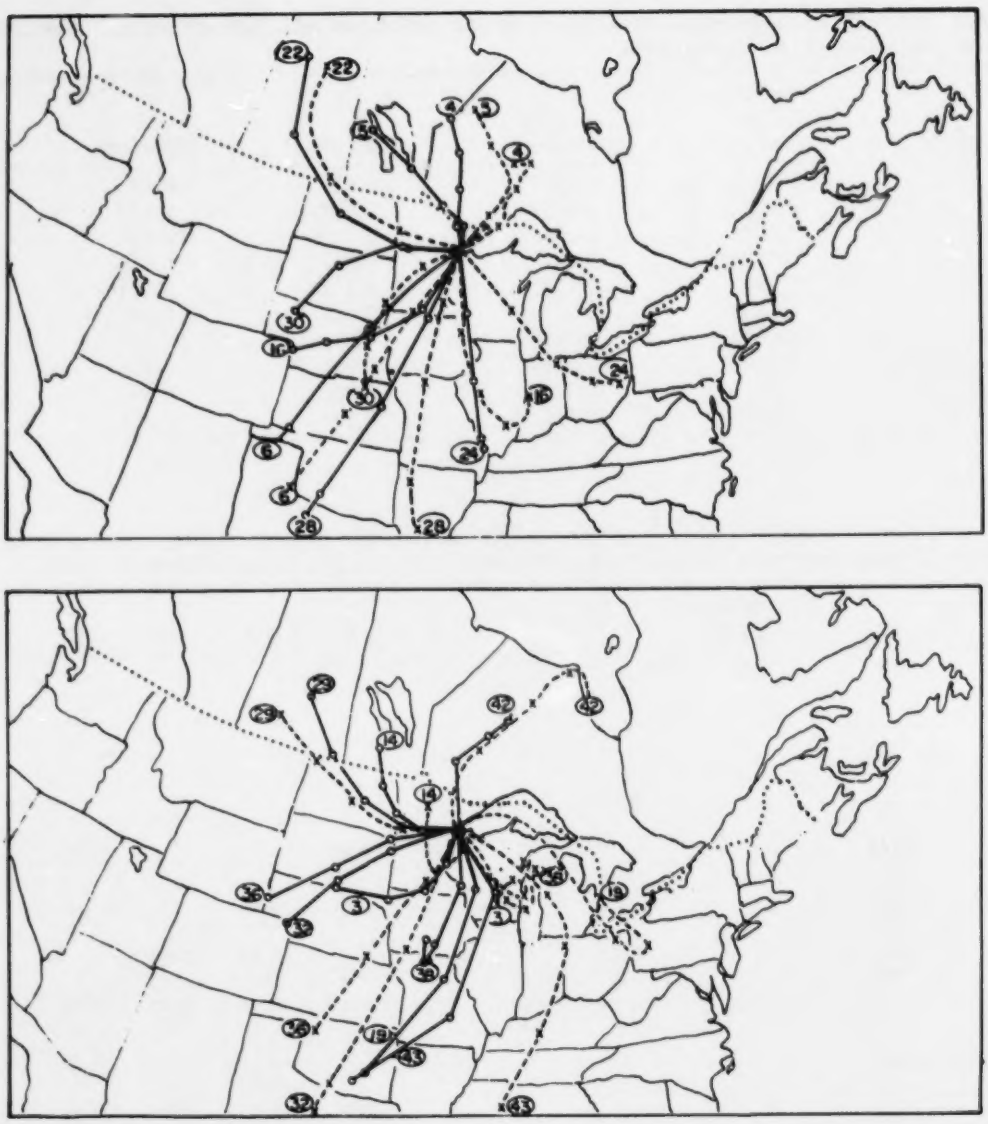

FIG. 3. Surface geostrophic (dotted lines) and upper atmospheric (850 mb, solid lines) air parcel back trajectories where the highest (upper figure) and lowest (lower figure) mercury concentrations in rain were observed. Label numbers refer to specific events listed in Table 4.

icant positive correlations with the elemental concentrations of S, B, Ca, Mg, Na, Fe, and Zn. These correlations may be interpreted cautiously in terms of the known and postulated atmospheric mechanisms of transport and transformations (Junge 1974, Brosset 1981 and 1983, Lindqvist *et al.* 1984). The strong positive correlations of mercury concentration with the soluble elemental components of precipitation S, B, and metals, and not with Si, is consistent with the observations and hypothesis that wet deposition rates and variability are linked with the oxidation/conversions of

TABLE 5. Summary of component concentrations in rain association with mercury concentrations for 28 samples during the period March–November, 1983.

Components	Mean Value (mg/L)	Standard Deviation	Median	Minimum	Maximum
S	0.72	0.38	0.62	0.19	1.85
P	0.024	0.0059	0.020	0.020	0.036
B	0.0084	0.0046	0.0065	0.005	0.025
Si	0.0526	0.061	0.037	0.030	0.355
Ca	0.284	0.234	0.247	0.024	1.14
Mg	0.0563	0.0289	0.040	0.040	0.157
Na	0.0680	0.0417	0.0505	0.040	0.209
Fe	0.0173	0.0246	0.011	0.003	0.133
Mn	0.0033	0.0030	0.002	0.001	0.014
Zn	0.0070	0.014	0.004	0.004	0.076

TABLE 6. Correlation coefficients and significance[1] for mercury and element concentrations in precipitation, and volume for 28 event samples at ERL-D, Duluth, Minnesota, from March through November 1983.

Parameter	Hg	Precipitation Volume	S	P	B	Si	Ca	Mg	Na	Fe	Mn
S	0.38 *										
P											
B	0.37 *										
Si			0.43 *	0.43 *							
Ca	0.48 **				0.39 *	0.45 *					
Mg	0.36 *		0.40 *		0.41 *	0.65 **	0.65 **				
Na	0.52 **		0.51 **		0.37 *	0.51 **	0.52 **	0.69 **			
Fe	0.41 *	–0.35	0.39 *	0.50 **		0.83 **	0.41 *	0.57 **	0.44 *		
Mn	0.36 *				0.43 *	0.47 **	0.82 **	0.70 **	0.49 **	0.38 *	
Zn	0.49 **	–0.41				0.31	0.31	0.34	0.55 **	0.55 **	

[1]Statistical significance of correlation compared with zero are indicated by ** for 0.99 to 1.00, * for 0.95 to >0.99, and blank for 0.90 to <0.95.

metallic mercury gas in the atmosphere to more water soluble compounds or particles that are then more effectively scavenged out of the atmosphere. The correlation of mercury with sulfur suggests the possibility of a direct mercury-sulfur interaction since mercury reactions with S are well known for their high degree of stability in the aquatic environment (Baughman *et al.* 1973). Additional data are needed on the specific chemical compounds of mercury present in the atmosphere to further interpret reaction and deposition mechanisms.

Significance of Mercury Concentration in Precipitation

The median concentration of total mercury measured in precipitation at Duluth, Minnesota, is higher than recommended for the protection of

aquatic life (USEPA 1980) and for human consumption if it is converted in surface waters into the chemical form most strongly bioaccumulated (Bishop and Neary 1974). Residue levels in fish from Lake Superior and some lakes within the region exceed the recommended levels for human consumption and are restricted (WDNR 1984, MDH 1985, MPCA 1985, MDNR 1985). The highest concentration events observed exceed direct toxicity concentrations for some aquatic organisms (USEPA 1980). The "toxicity potential" for mercury in wet deposition evaluated by Galloway *et al.* (1982) was found to be significant for levels observed at ERL-D.

Precipitation inputs of ionic and acid forming compounds and their impacts on surface waters were evaluated recently in the Upper Midwest by Glass and Loucks (1986). They found that the ionic composition of precipitation can dominate the major ion chemistry of surface waters in weakly buffered lakes. The precipitation inputs of mercury and lake water concentrations (Table 2) show a similar correspondence to that observed by Glass and Loucks (1986) for ionic and acid forming compounds, indicating that atmospheric inputs can have a major effect on lake water concentrations.

An evaluation of the mercury residue levels in fish from these lakes (Table 2) (Wiener *et al.* 1985) showed values exceeding 1.0 mg Hg/kg wet weight for pike, with increasing numbers of fish exceeding this residue limit for lakes with decreasing pH. Residue values in fish from some northern Minnesota lakes also exceed health criteria (Glass and Loucks 1980, MDH 1985), but additional studies remain to be done for these lakes with regard to conversion to biologically active organoforms and to determine contributions from sources other than the atmosphere. The present data seem to implicate atmospheric deposition as the major source of mercury to some lakes in the Lake Superior region, resulting in high residue levels in the aquatic biota.

SUMMARY AND CONCLUSIONS

Methodological investigations revealed that substantial losses of mercury from environmental samples (snow and precipitation) were observed where the preservative, $K_2Cr_2O_7/HNO_3$, was not present during storage or processing. The detection limit for the total mercury was improved to 0.013–0.008 μg/L by preselecting reagents of low mercury concentrations used in preserving samples and analyses and by using the gold gauze-amalgam procedure. Both deuterium arc and gold gauze procedures were used to check that no significant positive interferences were present.

Mercury was determined in rainfall events at the Environmental Research Laboratory-Duluth, Minnesota (ERL-D), and at Forbes and Dorset, Ontario. The mean value of total mercury concentrations at ERL-D for 44 events in 1982–1983 was 0.133 μg/L and ranged from 0.004 μg/L to 3.4 μg/L with a median value of 0.037 μg/L. Fifty four rain events were measured at Forbes and Dorset, Ontario, with concentration of mercury ranging $<$ 0.01 to 1.22 μg/L and $<$0.01 to 0.04 μg/L, respectively. The highest mercury concentrations were measured in June 1982 (3.4 μg/L) at ERL-D and July 1983 (1.22 μg/L) at Forbes, Ontario, and are comparable with the highest reported values (Galloway *et al.* 1982) for the urban areas of the U.S. and Canada (3.8 μg/L), and the median value in rain in the urban U.S. (0.74 μg/L).

The accumulation of mercury in the snow pack was significantly lower in concentration than in rainfall and was near detection limits with a mean concentration of about 0.014 μg/L at most sites. Regional comparisons show highest mean snow concentrations in the Grand Rapids, Minnesota, area, 0.10 μg/L, and lowest snow concentrations in the Hovland, Minnesota, and Atikokan, Ontario, areas.

The predominant air parcel back-trajectory pathways to Duluth during 1982 and 1983 were from the S, SW, W, and NW for the 44 precipitation events which were sampled. Highest mercury concentrations were associated with air parcel pathways from the NE to NW at both Duluth, Minnesota, and Forbes, Ontario. A strong seasonal trend indicated minimum mercury concentrations accumulated in snow and maximum mercury concentrations occurred in rainfall during spring and summer.

Mercury concentrations in rainfall and in lake water for precipitation dominated lakes are similar and indicate that atmospheric deposition may be the major source of mercury for some lakes in the Lake Superior region. Further, these concentrations are similar to those expected to result in fish residue levels unfit for human consumption.

Further study of air, rainfall, and snowfall mercury concentrations in conjunction with oxidants and chemical speciation are needed to: (1) identify the source(s) of airborne mercury, (2) determine

specific removal mechanisms and impacts on susceptible watershed sources, and (3) assess the significance of contributions from atmospheric deposition to aquatic biota already exceeding residue limits for human consumption for some lakes and streams in the Lake Superior region.

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REFERENCES

American Public Health Association 1981. *Standard Methods for the Examination of Water and Wastewater*. 15th Edition. American Public Health Association. Washington, D.C.

Baughman, G. L., Gordon, J. A., Wolfe, N. L., and Zepp, R. G. 1973. *Chemistry of Organomercurials in Aquatic Systems*. EPA-600/3-73-012.

Bishop, J. N., and Neary, B. P. 1974. The form of mercury in freshwater fish. In *Proc. Intl. Conf. on Transport of Persistent Chemicals in Aquatic Ecosystems*, pp. III25–III29. National Research Council of Canada, Ottawa.

Brosset, C. 1981. The mercury cycle. *Water, Air, Soil Pollut.* 16:253–255.

_____. 1982. Total airborne mercury and its possible origin. *Water, Air, Soil Pollut.* 17:37–50.

_____. 1983. Transport of airborne mercury emitted by coal burning into aquatic systems. *Water Sci. Technol.* 15:59–66.

Feldman, C. 1974. Preservation of dilute mercury solutions. *Anal. Chem.* 46(1):99–102.

Fogg, T. R., and Fitzgerald, W. F. 1979. Mercury in southern New England coastal rains. *J. Geophys. Res.* 84(C11):6987–6989.

Galloway, J. N., Thornton, J. D., Norton, S. A., Volchok, H. L., and McLean, R. A. N. 1982. Trace metals in atmospheric deposition: A review and assessment. *Atmos. Environ.* 16:1677–1700.

Glass, G. E. 1977. Identification and distribution of inorganic components in water: What to measure? *Ann. N.Y. Acad. Sci.* 298:31–46.

_____, and O. L. Loucks. 1980. *Impacts of Airborne Pollutants on Wilderness Areas Along the Minnesota-Ontario Border*. EPA-600/3-80-044.

_____, and O. L. Loucks. 1986. Implications of a gradient in acid and ion deposition across the northern Great Lakes states. *Environ. Sci. Technol.* 20:35–43.

Hartung, R., and Dinman, B. D. 1972. *Environmental Mercury Contamination*. Ann Arbor: Ann Arbor Science Pub.

Hogstrom, U., Enger, L., and Svedung, I. 1979. A study of atmospheric mercury dispersion. *Atmos. Environ.* 13:465–476.

International Joint Commission. 1980. *Seventh Annual Report. Great Lakes Water Quality*. International Joint Commission, U.S./Canada, Washington, D.C.

Junge, C. E. 1974. Residence time and variability of tropospheric trace gases. *Tellus* 26:477–488.

Lindqvist, O., Jernelov, A., Johansson, K., and Rodhe, H. 1984. *Mercury in the Swedish environment. Global and local sources*. National Swedish Protection Board, Solna, Sweden. SNV PM 1816.

Matheson, D. H. 1979. Mercury in the atmosphere and in precipitation. In *The Biogeochemistry of Mercury in the Environment*. J. Nriagu (ed.), pp. 113–129. Elsevier/North-Holland Biomedical Press.

Matsunaga, K., and Goto, T. 1976. Mercury in the air and precipitation. *Geochem. J.* 10:107–109.

Memorandum of Intent. 1983. United States-Canada Memorandum of Intent on Transboundary Air Pollution. Impact Assessment Work Group I. G. E. Bangay and C. Riordan, Co-chairmen. Final Report January, Department of State, Washington, D.C.

Michigan Department of Natural Resources. 1985. *Michigan Fishing Guide*. Michigan Department of Natural Resources, Fisheries Division, Lansing, MI.

Minnesota Department of Health. 1985. *Fish Consumption Advisory for Minnesota Waters*. Minnesota Department of Health. Minneapolis, MN. May.

Minnesota Pollution Control Agency. 1985. Fish Mercury in NE Minnesota Lakes. Minnesota Pollution Control Agency, Water Quality Division. Roseville, MN.

National Academy of Sciences. 1978. *An assessment of mercury in the environment*. ISBN 0-309-02736-5.

Olson, G. F., Mount, D. I., Snarski, V. M., and Thorslund, T. W. 1975. Mercury residues in fathead minnows chronically exposed to methylmercury in water. *Bull. Environ. Contam. Toxicol.* 14:129–134.

Ontario Ministry of the Environment. 1981. Outlines of analytical methods. Ontario Ministry of the Environ-

ment. Laboratory Services Branch. Toronto, Ontario, Canada.

Peterson, K. 1966. Estimating low-level tetroon trajectories. *J. Appl. Meteor.* 5:553–564.

Petterssen, S. 1956. *Weather Analysis and Forecasting.* Second Edition. Volume 1, pp. 27–30. Motion and Motion Systems. New York: McGraw-Hill.

Rahn, K. A. 1981. Mn/V ratio as a tracer of large-scale sources of pollution aerosol for the arctic. *Atmos. Environ.* 15:1457–1464.

Soil Conservation Service. 1967. *Snow-survey sampling guide.* USDA, Agriculture Handbook No. 169, Washington, D.C.

United States Environmental Protection Agency. 1979. *Methods for chemical analysis of water and wastes.* U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH. EPA-600/4-79-020.

_____. 1980. *Ambient Water Quality Criteria for Mercury.* Office of Water Regulations and Standards. Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/5-80-058.

Ure, A. M. 1975. The determination of mercury by nonflame atomic absorption and fluorescence spectrometry. *Anal. Chim. Acta* 76:1–26.

Wiener, J. G., Martini, R. E., Sheffy, T. B., and Glass, G. E. 1985. Factors influencing mercury contamination of walleyes in northern Wisconsin lakes. ERLD-993, in preparation.

Winefordner, J. D., and Long, G. L. 1983. Limit of detection: A closer look at the IUPAC definition. *Anal. Chem.* 55:712A–724A.

Wisconsin Department of Natural Resources. 1984. *Summary of Wisconsin fishing regulations.* Wisconsin Dept. Natural Resources. Pub. 4-1020(80), Madison, Wisconsin.

World Health Organization. 1976. Environmental Health Criteria I. Mercury. Geneva, Switzerland.

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